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The Combustion of Ammonium Perchlorate - Based Composite Propellants: A Discussion of Some Recent Experimental Results

J. Powling

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REPORT NO. 15/R/65

I
The Combustion of II Ammonium Perchlorate-Based
Composite Propellants A Discussion of
Some Recent Experimental Results

by
III
J. Powling

1. Propellants, Composite.

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1. SUMMARY

Current experimental studies, at E.R.D.E. and elsewhere, on various aspects of the combustion of ammonium perchlorate-based propellants are discussed in relation to an accepted model for composite propellant burning.

The nature of the chemical processes taking place at the solid/gas interface and the possibility of heat release in the condensed phase are considered. A summary of the results of surface temperature measurements on ammonium perchlorate burning under a variety of conditions from 0.8 to 300 p.s.i.a. is presented. Although the evidence is that some heat release is likely to occur within the solid surface, the combustion in all pressure regions appears to be dominated by gas phase reactions. Results with catalysts which are supposed to increase the extent of the condensed phase reaction do not alter this conclusion.

For most practical propellants burning in the "low pressure" region, the burning rate is probably controlled by a homogeneous premixed gas phase reaction between ammonia, perchloric acid and fuel pyrolysis products. Its very low activation energy is associated with the perchloric acid/fuel reaction; the precise nature of the organic fuel is unimportant. This is in distinct contrast to the strong effect of the chemical nature of the binder in the high pressure region. Some of the possible reasons for this have been explored experimentally, including the penetration of flame down the binder/oxidiser interface and the effect of the thermal stability of the fuel-binder. Some results from experiments on closed vessel pyrolysis of a variety of polymeric fuels are presented.

2. INTRODUCTION

In this report a qualitative model for the combustion of ammonium perchlorate-based composite propellants is outlined and certain features of the model are examined in the light of some new, or recently published, experimental findings. This model derives from the studies and proposals of many workers in the field, principally R. Friedman and J.B. Levy, M. Summerfield et al, S.S. Penner, W. Nachbar, G.K. Adams et al, and Anderson and Chaiken. (Comprehensive reference to previous publications has not been attempted but particular reference to the work of Summerfield and his co-workers (1a, 1b), and to the useful review by Friedman and Levy (2) is made.) The model provides a framework for the discussion of some experimental details. Theoretical analyses, mostly of grossly simplified models, often involve assumptions which have no direct backing of experimental evidence, and it is left to the experimentalist to endorse, or otherwise, the predictions or particular features of a model, in retrospect. So it is

/desirable

desirable at intervals to examine how far current experimental data will support a model, and what modifications are required to accommodate new observations.

3. MODEL OF PLASTIC PROPELLANT FLAME

In order to be reasonably specific regarding, for example, the kind of flame that is characteristic of a given pressure, we will consider a typical plastic propellant (11 per cent polyisobutene binder, 89 per cent ammonium perchlorate) with a nominal perchlorate particle diameter of 30 microns. Figures 1A and 1B give a diagrammatic representation of the types of flame, and their temperature profiles, visualised for such a composition in three of the characteristic pressure regions indicated by Bastress (1b) and by Barrère and Nadaud (3). To give slight dimensional significance to the model in Figure 1A, the thicknesses of the low-pressure premixed flames and the ammonium perchlorate decomposition flame, indicated in the figures, were roughly estimated as follows. The (known) final flame temperature, T_f is assumed to be located at a distance, x , from the surface (at temperature, T_s) such that the heat flux (q) to the surface is sufficient to gasify the condensed phase at the observed linear regression rate

$$x = \frac{\lambda(T_s - T_f)}{q}$$

λ is the thermal conductivity of the reactant gases at a mean temperature.

The distance required for mixing of the fuel and oxidiser gas streams, or the diffusion flame height, h , is roughly estimated from

$$h = \frac{Vd^2}{8D}$$

where D = a nominal gaseous diffusion coefficient at $T = (T_f + T_s)/2$

V = average gas velocity

d = diameter of the ammonium perchlorate particles.

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The effect of temperature and pressure on the diffusion coefficient and gas velocity is assumed to be according to:

$$D = D_0 \left(\frac{T}{T_0} \right)^2 \frac{P_0}{P}$$

$$V = V_0 \frac{T}{T_0} \frac{P_0}{P}$$

where D_0 = diffusion coefficient at s.t.p.

V_0 = gas velocity calculated for s.t.p.

Hence

$$h = \frac{V_0 d^2 T_0}{8 D_0 T}.$$

If it is assumed for simplicity that there is no heat release in the condensed phase it can be estimated from the heat flux required to vaporise the solid that the flame thickness of a typical plastic propellant at atmospheric pressure is likely to be of the same order as the average particle size of the ammonium perchlorate incorporated (10 - 100 microns). The thickness would increase to about 1000 microns at 100 mm Hg, this estimate agreeing with the observed thickness of the chemiluminescent zone (21). Summerfield et al. (1a) have recorded experimentally gas phase reaction zones of ~100 microns for composite propellants at atmospheric pressure and Povinelli (22) has observed that CN emission from a composition burning at one atmosphere begins at ~70 microns and reaches a maximum at <235 microns. The AP decomposition flame at 1000 p.s.i. is probably less than 1 micron thick.

At a few atmospheres pressure and below, the time required for inter-diffusion of fuel pyrolysis products and oxidiser dissociation products is short compared with the time for chemical reaction and the premixed flame of $\text{NH}_3/\text{HClO}_4$ /fuel gases controls the rate of burning.

In the neighbourhood of 300 p.s.i. the decomposition flame of $\text{NH}_3 + \text{HClO}_4$ is probably stable and located within a few microns of the ammonium perchlorate surface, and, although it may contain little of the fuel pyrolysis products, it is strongly influenced by the close diffusion flame involving the reaction of its products, O_2 , Cl_2 , NO , N_2O , etc., with inter-diffusing fuel pyrolysis products.

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In the high pressure region, say above 1000 p.s.i., the ammonium perchlorate decomposition flame is rapid, self-sustained and located less than 1 micron from the surface. It is presumed to control the burning rate by being a rapid, independent process and the influence of the relatively remote diffusion flame is considered to be secondary.

The pressure limits for these three principal regions depend very much upon the oxidiser particle size and in practical propellants the boundaries must be expected to be very diffuse (1b, 3).

4. CONDITIONS AT THE BURNING SURFACE

The nature of the chemical reactions controlling the combustion of ammonium perchlorate still remains largely a matter of conjecture and although there is a large body of work on the thermal decomposition of the salt, which might be expected to give an insight to these reactions, its relevance has always been in some doubt. Consistent interpretation of low temperature pyrolysis data had not, until recently, been achieved and the temperature conditions at the deflagrating perchlorate surface were unknown. Many of the anomalies in the pyrolysis data have now been eliminated (4) and infrared radiation measurements have established the surface temperature conditions of the perchlorate for a (limited) range of conditions of fuel concentration, fuel composition, and pressure (5,6).

It seemed likely on the evidence of invariance of surface temperature with burning rate (1 atmos.) (6) and the variation of surface temperature with pressure (6,19) that the process taking place at the solid/gas interface was that of near-thermodynamic equilibrium between the crystalline ammonium perchlorate (AP) and its dissociation products, gaseous ammonia and perchloric acid.



$$\Delta H = 58 \text{ kcal/mole.}$$

If equilibrium exists between solid and gaseous phase at the burning surface, the surface temperature is determined essentially by the ambient pressure

$$K_p = p_{\text{NH}_3} \times p_{\text{HClO}_4} = aP^2$$

/and

and
$$\ln \left(\frac{K_{p1}}{K_{p2}} \right) = 2 \times \ln \left(\frac{P_1}{P_2} \right) = \frac{\Delta H_s}{R} \left(\frac{1}{T_{s2}} - \frac{1}{T_{s1}} \right)$$

where K_p = equilibrium constant for reaction

p = partial pressure

P = ambient pressure

ΔH_s = heat of dissociation of ammonium perchlorate

T_s = surface temperature

a = assumed constant.

On the other hand, if the reverse Reaction 1b is unimportant, then the surface temperature is directly related to burning rate which, at low pressure, is found to be directly proportional to the ambient pressure, P (not P^2):

$$\begin{aligned} R_b &= b P^n \quad (n = 1 \text{ at low pressures}) \\ &= c k_{1a} \end{aligned}$$

$$\ln \left(\frac{k_1}{k_2} \right)_{1a} = \frac{E}{R} \left(\frac{1}{T_{s2}} - \frac{1}{T_{s1}} \right)$$

where R_b = rate of burning

n = pressure exponent of burning rate

k_{1a} = rate constant for reaction 1a.

It was found (6) that the rates at atmospheric pressure could not be described by an Arrhenius expression involving T_s unless the activation energy for the decomposition were so high that the variation of T_s , for the limited range of rates obtainable, was too small to be reliably detected. The low activation energy ($E \approx 22000$ cal/mole) derived from the linear pyrolysis of AP (7) was not compatible with the results and it was considered

/that

that the temperature increase required by an activation energy of 60 kcal/mole or less should be easily detected. However, McAlevy and Lee (8) using a thermocouple technique have shown a distinct variation of surface temperature with burning rate for porous beds of ammonium perchlorate burning in a flow of methane at 40 mm Hg, a result in conflict with the idea of equilibrium dissociation of the perchlorate. Therefore, using the infrared radiometric method we also determined the surface temperature of beds burning under similar conditions and at fixed pressures in the range 40 to 760 mm Hg and, although we do not agree over the level of temperatures involved, we also detected a variation in surface temperature at constant (low) pressure. This variation diminishes with increase in pressure level and is very small at 1 atmosphere. Apart from the observed lack of variation of T_s with burning rate at constant pressures near atmospheric, the new experimental data up to atmospheric pressure may indeed be reasonably well fitted by a kinetic decomposition equation with $E \approx 30$ kcal/mole. The question of whether equilibrium Reaction 1 is maintained under different conditions remains open, therefore, but the new data, summarised in Figure 2, will be considered in detail in a later report.

Although it is now appreciated that equilibrium dissociation is likely to represent an oversimplification of conditions obtaining at the surface, we can with some confidence assume that Reaction 1 remains valid, with the relative rates of dissociation (1a) and combination (1b) depending on conditions, and subject to the reservations below.

The recent thermogravimetric data of Jacobs and Russell-Jones (4) have shown that at constant temperature the rate of decomposition of that fraction of ammonium perchlorate (nominally 30 per cent) which normally decomposes in the "low temperature" region (below 300°C) would be competitive with rate of vacuum sublimation, Reaction 1a.

The rate constants for the different phases of reaction are as follows:

low temperature decomposition

$$k = 10^{11.51} \exp\left(\frac{-31,300}{RT}\right) \text{ min}^{-1}$$

high temperature decomposition

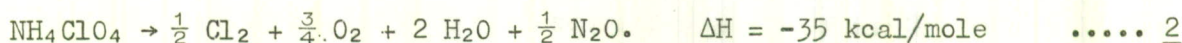
$$k = 10^{8.59} \exp\left(\frac{-30,600}{RT}\right) \text{ min}^{-1}$$

/vacuum

vacuum sublimation

$$k = 10^{11.26} \exp \left(\frac{-30,300}{RT} \right) \text{ min}^{-1}.$$

It might be expected that a significant degree of degeneration, according to the low temperature Reaction 2 below, might accompany sublimation under flame conditions.



The presence of N_2O in the flame gases (see Table 1, p. 9) has been considered as evidence for the occurrence of this reaction in combustion. If the quantity is taken as a measure of the degree of decomposition via Reaction 2 it would indeed correspond to 20 to 30 mole per cent of the perchlorate at a combustion pressure of one atmosphere. However, we find that ammonium perchlorate, from which all the "less stable" material has been removed by heating above 270°C , also gives N_2O so the evidence is inconclusive. Jacobs has concluded that Reaction 2 is a solid phase decomposition; as such it could be most important in the combustion process, since it represents a source of heat within the surface layer. It becomes a major competitive source of energy release if the products on or near the surface are sufficiently reactive (e.g. $\dot{\text{Cl}}$ or $\dot{\text{O}}$) to combine with adjacent fuel elements before the onset of homogeneous gas phase reaction of NH_3 , HClO_4 and fuel gases.

Anderson, Brown and Shannon (9) believe that such heterogeneous reactions are rate-controlling in the ignition phases of composite propellant burning and also play a dominant role during deflagration, in accord with their view that the combustion of ammonium perchlorate propagates by ignition and subsequent burning of each individual particle (10).

We also believe that this concept of ignition of each individual oxidiser particle is important in the determination of the burning velocity of composite propellants in the high pressure region where the decomposition flame thickness is small compared with particle dimensions. The chemical nature of the fuel binder then becomes important with regard to its ability to assist or retard the ignition processes of the oxidiser. However, it would be difficult to distinguish between spontaneous ignition of each particle and, for example, the spread of the reaction wave along binder/oxidiser interfaces or via points of direct contact of oxidiser crystals. Undoubtedly, such unsteady phenomena can explain many of the complex features of the burning of ammonium perchlorate/fuel mixtures in the high pressure region say >1000 p.s.i. (see Sections 7 and 8).

/Direct

Direct evidence of heterogeneous reactions and heat release in the condensed phase is difficult to establish, but on the strength of temperature profiles obtained from thermocouple measurements, Russian workers (11) show a substantial condensed-phase heat release for pure AP at high pressures, as do Sabadell, Wenograd and Summerfield (12) for composite propellants at intermediate pressures.

The evidence, however, is only valid if it can be shown that the thermocouples follow closely the temperature course in both the condensed phase and the gas phase. If the thermal lag in the gas phase is greater than that in the condensed phase (as is likely), there will appear to be a heat release in the solid. The Russian workers have been at pains to explain an apparent fall in the surface temperature with increase in burning rate and pressure, together with a large apparent heat release in the solid. We feel that these data, derived from thermocouple measurements, should be treated with caution and examined in conjunction with some estimate of the appropriate temperature gradients. Figure 3 shows the dimensions of the thermocouple junction used by the different authors and the approximate condensed-phase temperature gradients which the detectors were expected to record. More direct and remarkable evidence for condensed-phase reactions has been provided by Wenograd (13) who recently demonstrated that an ammonium perchlorate-based propellant can undergo, at very low pressures, a self-sustained, low temperature ($\sim 300^{\circ}\text{C}$) decomposition in which only a part of the oxidiser and fuel, is consumed. This might well be associated with the "low temperature" phase of the thermal decomposition of ammonium perchlorate which occurs below $\sim 300^{\circ}\text{C}$ (Reaction 2) and subsequent heterogeneous reaction of oxidiser gases and fuel elements. Since this oxidiser decomposition is an exothermic solid phase reaction (4), it is conceivable that it might sustain a reaction wave at pressures below those at which the usual gas phase reactions are quenched.

We have observed that ammonium perchlorate, containing ~ 3 per cent calcium carbonate but without fuel or preheat, can undergo a self-sustained decomposition even at atmospheric pressure. This flame is distinctive in that it is controlled by a condensed phase decomposition of the perchlorates in a molten surface layer. The liquid surface temperature is about 400°C and the maximum gas temperature little different. The nitrogenous products of this "fizz burning" of ammonium perchlorate are predominantly N_2O . (If small quantities of fuel are added to this system, the condensed phase reaction becomes erratic and burning may be extinguished by a mild explosive dispersal of the molten layer. With larger quantities of fuel, the gas phase reaction dominates and no accumulation of molten surface reactants takes place.) Analyses of products of ammonium perchlorate decomposition flames are given in Table 1.

/TABLE 1

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TABLE 1
Ammonium Perchlorate Flame Products (Atmospheric Pressure)*

Fuel	Nil	3.85% (H ₂ CO) _n	3.85% (H ₂ CO) _n	Nil	Nil	Nil	Nil	Nil	Nil
Catalyst	Nil	Nil	2.9% CC†	2.9% CC	2.9% Al ₂ O ₃ †	2.9% CaCO ₃	2.9% CaCO ₃	2.9% CaCO ₃	2.9% CaCO ₃
Product	Moles per 100 moles of ammonium perchlorate								
H ₂ O	198	188	225	192	166	176	199		
O ₂	73	63	80	87	68	103	32		
NO	54	50	24	42	69	42	9		
HCl	30	29	36	39	25	29	15		
N ₂	8.5	8.5	28	17	7	17	22		
Cl ₂	35	32	25	29	39	25	43		
N ₂ O	14	13	9	6	11	15	47		
CO ₂	-	(15)	(10)	-	-	-	-		
CO	-	(8)	(3)	-	-	-	-		
Initial temperature (°C)	280	20	20	250	280	280	60		
Flame temperature (°C)	970	1100	> 940	900	875	-	~400		
* Some of these analyses were given in an earlier publication (14.)									
† Inactive									
‡ Copper chromate									
Normal flame burning									
"Fizz burning", condensed phase decomposition, liquid surface temperature 400°C									

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In the light of the above evidence it would seem unrealistic to discount the condensed-phase decomposition, Reaction 2, as a parallel to the dissociation Reaction 1, in the primary combustion process. The extent to which Reaction 2 might occur in combustion remains difficult to predict; under isothermal conditions it is limited to about 30 per cent.

5. GAS PHASE REACTIONS IN THE LOW PRESSURE REGION

Since the rate of vacuum sublimation (Reaction 1a), is faster than that of reactions controlling the "high temperatures" phase of AP decomposition, gasification will occur before redox reactions take place. The pressure exponent of burning rate for most AP/solid fuel mixtures is close to unity in the sub-atmospheric pressure region, (and for fuel-weak mixtures up to ~1000 p.s.i.) indicating that a bimolecular gas phase reaction is rate-controlling.

It is interesting to make another comparison between the results of the closed vessel pyrolysis work and those from flame experiments. Jacobs and Russell-Jones find that the activation energy of the complex gas phase reactions leading to ignition of (catalysed) AP is about 12 - 14 kcal/mole and a similarly low activation energy (15 kcal/mole) has been obtained for the perchloric acid gas/hydrogen flame by Cummings and Pearson (15). From ignition delay data for practical ammonium perchlorate propellants Sutton and Wellings (23) derive activation energies of 5.5 to 10 kcal/mole for uncatalysed compositions and rather higher values (10 to 11 kcal/mole) for those containing catalyst. Kling, Maman and Buland (24) also remark on the low activation energy (4,600 cal/mole) they derive for the ignition of composite propellants. It can be shown that at atmospheric pressure the primary flame of the mixtures of 90 micron diameter AP with readily-gasified fuels is virtually homogeneous and premixed and so an estimate of the overall activation energy, assuming a bimolecular controlling reaction, can similarly be obtained from available flame temperature and burning rate measurements (14). Irrespective of the precise nature of the organic fuel, these data also indicate a very low activation energy of about 11 kcal/mole, (Figure 4). In contrast, the decomposition flame of perchloric acid without fuel gave (15) a much higher activation energy (45 kcal/mole) corresponding to the perchloric acid thermal decomposition value. The independence of burning rate and precise chemical nature of the fuel extends to mixtures of near-stoichiometric proportions if the AP is finely divided. Compared at approximately constant final flame temperature (2700° - 2800° K) the burning rates of ammonium perchlorate (weight average diameter ~30 microns) with a variety of fuels are remarkably similar at atmospheric pressure (Table 2). Markedly different behaviour is found in the high pressure region.

/TABLE 2

TABLE 2

Fuel	Burning Rate [‡] (cm/sec)
23% polyester polyurethane rubber	0.11
23% polyester (uncrosslinked)	0.10
20% polypropylene glycol polyurethane rubber	0.11
20% polypropylene glycol	0.11
16% polystyrene	0.093
14.3% polyisobutene	0.104
20% polyvinyl alcohol [†]	0.112
20% paraformaldehyde	0.10
18% polymethyl methacrylate	0.107
25% polyvinyl chloride [†]	0.094

[‡]Strand diameter >1 cm. cylindrical surface, inhibited and burned in air: T_f 2700° - 2800°K.

[†] T_f uncertain.

With gaseous fuels of low and widely differing molecular weights passing through beds of coarser AP grains (250 - 540 μ) Burger and Van Tiggelen (16) and ourselves find that burning rate at atmospheric pressure depends more strongly upon the nature of the fuel but in these cases the relative diffusivities and flame temperature distribution become important; the "mixed", or "granular diffusion" flame region has been entered.

Barrère and Nadaud (17) considering the combustion of single, 6 mm diameter, AP spheres in gaseous atmospheres at moderate pressures (up to 220 p.s.i.) state that regression rates are controlled by the nature of the fuel gas and hence by the diffusion flame surrounding the oxidiser sphere, and (at least for fuel atmosphere of NH_3 and C_3H_8) the process is quite analogous to the combustion of fuel droplets in air. A complex and variable

/visible

visible flame structure is observed (depending upon the nature of the fuel) but a discrete decomposition flame is not always apparent. They state that the mass burning rate is controlled by the diffusion flame rather than by the decomposition flame located close to the surface. Extensive premixing of fuel gas into the decomposition flame zone would not be expected with large spheres of ammonium perchlorate, whereas this is likely with the AP sizes used by Berger and Van Tiggelen (16). With these large spheres of perchlorate Barrère and Nadaud find pressure exponents of about one half, whereas in the same pressure region and with finer particles (say ~30 microns diameter) pressure exponents of near unity are common with all kinds of fuel. There is no reason why the general, low pressure, combustion characteristics of porous beds of ammonium perchlorate should differ from compositions containing solid fuels provided the latter gasify reasonably readily. It can be shown from fuel pyrolysis rates and the heat fluxes expected within the burning surface that, for example, at atmospheric pressure, paraformaldehyde should gasify well below the perchlorate surface, and polyisobutene and polyurethane rubbers in about the same surface plane as the oxidiser.

Under the conditions established by Barrère and Nadaud, with the large spheres of AP, the decomposition flame ($\text{NH}_3 + \text{HClO}_4$) is maintained by a subsequent diffusion flame (O_2 , Cl_2 , $\text{NO} + \text{fuel gas}$) and is, as they suggest, more representative of higher pressure, composite propellant burning than the pressures presently being considered, where premixed fuel gas can take part in the rapid perchloric acid flame. At sufficiently high pressures the decomposition flame is likely to be largely independent of subsequent diffusion flames. The mass consumption rate of an "infinite slab" of ammonium perchlorate (in practice a 1 inch diameter pressed cylindrical pellet) burning at one atmosphere pressure in a counter-flow diffusion flame with a hydrogen/nitrogen gas mixture as the fuel (5), ranges from $0.01 - 0.02 \text{ g/cm}^2$ (no "premixing" of fuel gas is possible with this arrangement) whereas the rates of burning of the porous beds of 190 - 250 micron ammonium perchlorate (our work) and 250 - 540 micron material (Berger and Van Tiggelen) are greater by an order of magnitude.

The atmospheric pressure burning rate of the porous beds using the higher molecular weight fuel gases (e.g. CH_4 , C_3H_8 , C_5H_{12}) were the same as those for practical propellants of similar stoichiometry and flame temperature.

Berger and Van Tiggelen concluded that a pure diffusion flame model would not account for their results at atmospheric pressure and considered that a premixed fuel gas/ NH_3 / HClO_4 controlling flame is more probable.

In the light of the general evidence summarised above, it seems reasonable to assume that the burning rate of most composite propellant mixtures, at low pressures, say below 300 p.s.i., is controlled by a fast premixed flame, the low activation energy of which is characteristic of perchloric acid/fuel gas reactions (but not the perchloric acid decomposition flame). Friedman and

/Levy (3)

Levy (3) predicted that perchloric acid decomposition of itself would be too slow to determine flame speed, and elsewhere in their review estimate that the rate of a corresponding hydrocarbon/air flame would be much too slow to account for the low pressure burning rate of AP-based propellants. The anomaly is dispelled by the characteristic high velocity observed for premixed HClO_4 /fuel flames.

Excepting the possible heat release in the condensed phase by Reaction 2, the precise condition of the AP surface does not (at low pressures and in the absence of catalysts) seem to be of any great significance as far as burning rate control is concerned. It is nevertheless an important stage in the overall reaction and needs to be understood, particularly as there is evidence that distinct changes in the surface structure occur when burning rate catalysts are added to the system (14); ammonium perchlorate will burn without added fuel at atmospheric pressure if sufficient catalyst is added. Evidence from numerous differential thermal analysis and other studies of AP/catalyst systems suggest that many positive burning rate catalysts increased considerably the extent of the fast "low temperature" decomposition (Reaction 2) of ammonium perchlorate. If this were indeed the case then burning rate controlling reactions might be located in the condensed phase when catalysts were present. However, Jacobs and Russell-Jones find that it is the "high temperature" reaction which is most influenced by catalysts. Under the influence of catalysts the rate of the "high temperature" reaction is so enhanced that it may become competitive with the "low temperature" reaction so that, for example, both could proceed at the 270°C exotherm. Moreover, the pressure exponent of burning rate of AP/fuel mixtures (in the low pressure region) is little affected by catalysts and remains close to unity (Figure 5), supporting the idea that the same gas phase reactions are rate-controlling in the presence of catalysts. The addition of catalysts to composite propellants (in contrast to AP without fuel) rarely makes a large difference to the pressure exponent in any pressure region. This is perhaps surprising since the character of the combustion process appears, at least at low pressures, to change markedly (14). Reaction waves of enhanced luminosity move across the burning surface and local fluctuations of the gas temperature and the surface temperature may be recorded, Figure 6.

6. DELAYED OXIDATION PROCESSES

Complex flame structures (e.g., those observed by Barrère and Nadaud, and the plateaux in thermocouple measurements by Sabadell, Wenograd and Summerfield) in addition to those due to varying degrees of inter-diffusion of fuel gases, are to be expected as a result of the widely different stabilities of the oxidising gases produced in the flame decomposition of AP (see Table 1). The oxidising reactions of chlorine oxides (from HClO_4) are likely to be much faster than those of oxygen which in turn are faster than those of nitric oxide. Two-stage flames of $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ /fuel gas have been observed (18), indicating the different reactivity of chlorine oxide and oxygen, and the delayed oxidation reactions in systems producing NO (e.g.

/nitric

nitric ester combustion) are very well known. Thus a three-stage oxidation sequence is credible in ammonium perchlorate/fuel systems even burning in the "premixed" flame region. If analogy with the nitric ester system can be made, the reactions of nitric oxide will begin to merge with those of oxygen as the pressure and flame temperature increase.

7. THE "MIXED FLAME" REGION

New experimental results in the intermediate pressure range (granular diffusion flame region of Summerfield) apart from burning rate measurements, remain very meagre because of practical difficulties. Measurements of the burning surface temperature of ammonium perchlorate have been made (19) for pressures up to 300 p.s.i. (Figure 7) and the change of T_s with pressure has been interpreted on an equilibrium dissociation basis (Reaction 1).

The burning rate laws established by Barrère and Nadaud for large ammonium perchlorate spheres, as a function of ambient gas composition, pressure and flow rate, are probably appropriate to this combustion region. These authors conclude that the diffusion flame, rather than the perchlorate decomposition flame, is rate-controlling up to say 30 atmospheres. With the large spheres employed, however, analogy with composite propellant combustion in a given pressure region is not too direct. The decomposition flame requires only a minor addition of heat to be fast and stable at atmospheric pressure (about 100 cal/g. added by radiation, preheat or added fuel) and if the reduction of reaction product, NO, is sufficiently rapid (e.g. at high pressures or under the influence of catalysts) no extra stimulus is necessary. Contrary to Barrère and Nadaud we consider, therefore, that it is likely to be an important phase of reaction in all pressure regions even if it is not, by itself, necessarily rate-controlling.

The importance of "flash back", or flame travel around the outside of each oxidiser crystal, is brought out visibly by the study of these large spheres. We also consider it important in the burning of practical propellants. If flame travel around crystals and along interfaces is faster than the "normal" burning velocity it could, in certain pressure regions, dominate the burning process by increasing burning surface area and by isolating and dispersing unreacted oxidiser particles and binder globules into the gasphase (compare the ejection of unreacted aluminium globules from the burning surface of propellants). Such a phenomenon might account for the liberation of the "fuel pockets" (Summerfield theory) or "oxidiser pockets" (Penner (20) interpretation) which are required to be consumed by a diffusion process above the burning surface in order to account for the observed pressure dependence of burning rate. The subject deserves study in relation to flame thickness and flame quenching distances, binder/oxidiser interface reactions, flash-down in porous propellants and the activity of catalysts at high pressures.

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We have been measuring the rate of flame travel down single binder/ammonium perchlorate interfaces as a function of pressure, and although no remarkably high penetration rates have so far been measured (Figure 8), provided the surfaces are well bonded, the physical condition of binder pyrolysis products appears to be of importance. Relatively stable liquid products from the pyrolysis of certain binders appear to be able to inhibit flame penetration, presumably by effectively wetting AP surfaces and filling potential crevices. Inert additives such as extremely fine silica powder, which can "hold up" liquid products can exert a powerful influence on flame penetration and on propellant burning rate (Figure 8a). This phenomenon appears to be another demonstration of the importance of surface melting on burning rate, which is common to the burning of high explosives (25) and propellants.

8. THE HIGH PRESSURE REGION

The phenomenon of flame travel along interfaces may account for the unexpected behaviour of certain compositions in the high pressure region (above, say, 1000 p.s.i.). In this region we assume that the decomposition flame of ammonium perchlorate is fast and can proceed without dependence on contribution from the fuel oxidation process. Somewhat paradoxically, the chemical nature of the fuel seems to be of greater importance in the high pressure region than in the low pressure region. Depending upon the nature of the fuel, the basic burning rate of ammonium perchlorate can be increased or decreased by fuel addition. Figure 9 compares (at constant final flame temperature and oxidiser particle size) the burning rates of compositions containing different fuels. Whereas at ambient pressure all the compositions burn at virtually the same rate, above 1000 p.s.i.g. the rates may vary by a factor of four or more.

As a starting point for the interpretation of results we assume that, at high pressures, the burning rate is determined primarily by the ammonium perchlorate decomposition flame. The temperature of this flame, and the overall burning rate, can be enhanced at least at binder/oxidiser boundaries by the diffusion flame of oxidiser products and fuel pyrolysis products. On the other hand, flame propagation may be inhibited by the barrier of fuel between oxidiser crystals, and any agent which assists the transmission of flame from one crystal to another would be an effective rate catalyst. We have therefore been seeking a correlation between high pressure burning rates (Figure 9) and fuel-binder thermal stability (Figure 10) on the broad assumption that, at constant final flame temperature the positive contribution of all the binders to burning rate would be about the same but the impediment to flame transmission might vary inversely as their ease of gasification.

Relative thermal stabilities, and pyrolysis characteristics are being measured in furnaces (26) and in diffusion flames (27); typical furnace data are given in Figure 10. As yet, no basis for the general correlation of

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burning rate data and pyrolysis characteristics has become apparent. We believe that, apart from thermal stability, important factors include the volumetric loading of the binder, the possibility of melting and the formation of carbon in the condensed phase.

Involatile, but finely particulate fuels (e.g., carbon, aluminium) which do not impede flame transmission, contribute more to burning rate at high pressures than at low pressures. The degree of actual contact between oxidiser crystals may be more important than the mean thickness of the fuel barrier separating crystals. Transverse gas velocities most noticeably enhance the burning rates of those propellants in which a fuel barrier would be expected: the high binder-content propellants used by Bastress et al. (1b) and our polyester polyurethane compositions containing 20 per cent or more binder frequently will not maintain steady deflagration to high pressures in the stagnant atmosphere of a strand burner whereas no such burning problems are encountered in motors. Bearing in mind the concept of a fuel barrier between oxidiser crystals it is interesting to note how difficult it is to prevent flash-down in pressed pellets of particulate polymeric fuels and oxidiser in near-stoichiometric proportions. In these pellets continuity of the binder element is less likely than in correctly mixed propellant. Flash-down rates can be extremely high, many times the basic burning rate of ammonium perchlorate, but nothing is known of the mechanism in composite propellants. We assume that interconnected gas spaces are necessary but the width of these at pressures above 1000 p.s.i., need be no more than, say, one micron to allow flame penetration, the thickness of the ammonium perchlorate decomposition flame being about one to one tenth of a micron thick.

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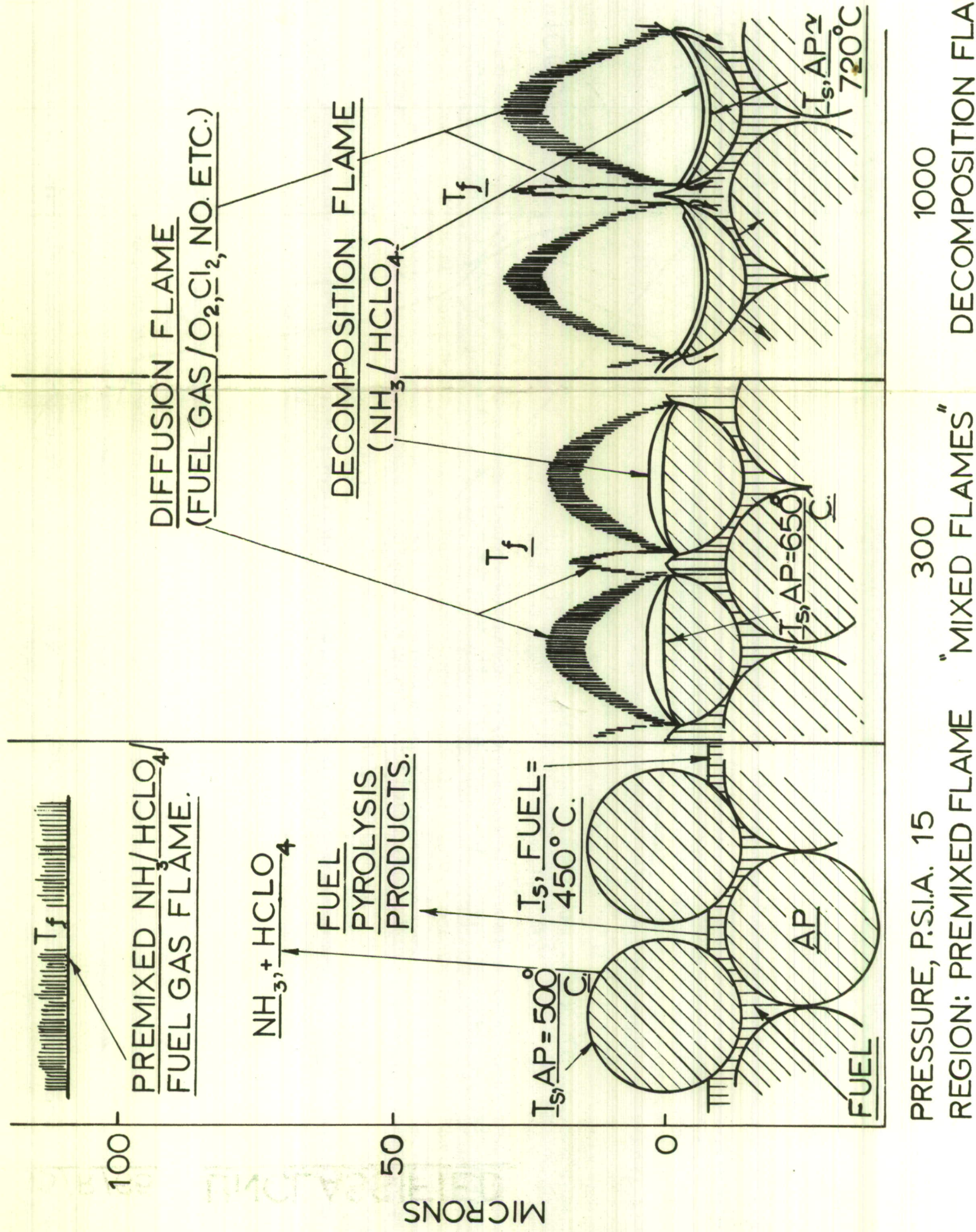


FIG.1A. FLAME MODEL FOR PLASTIC PROPELLANT

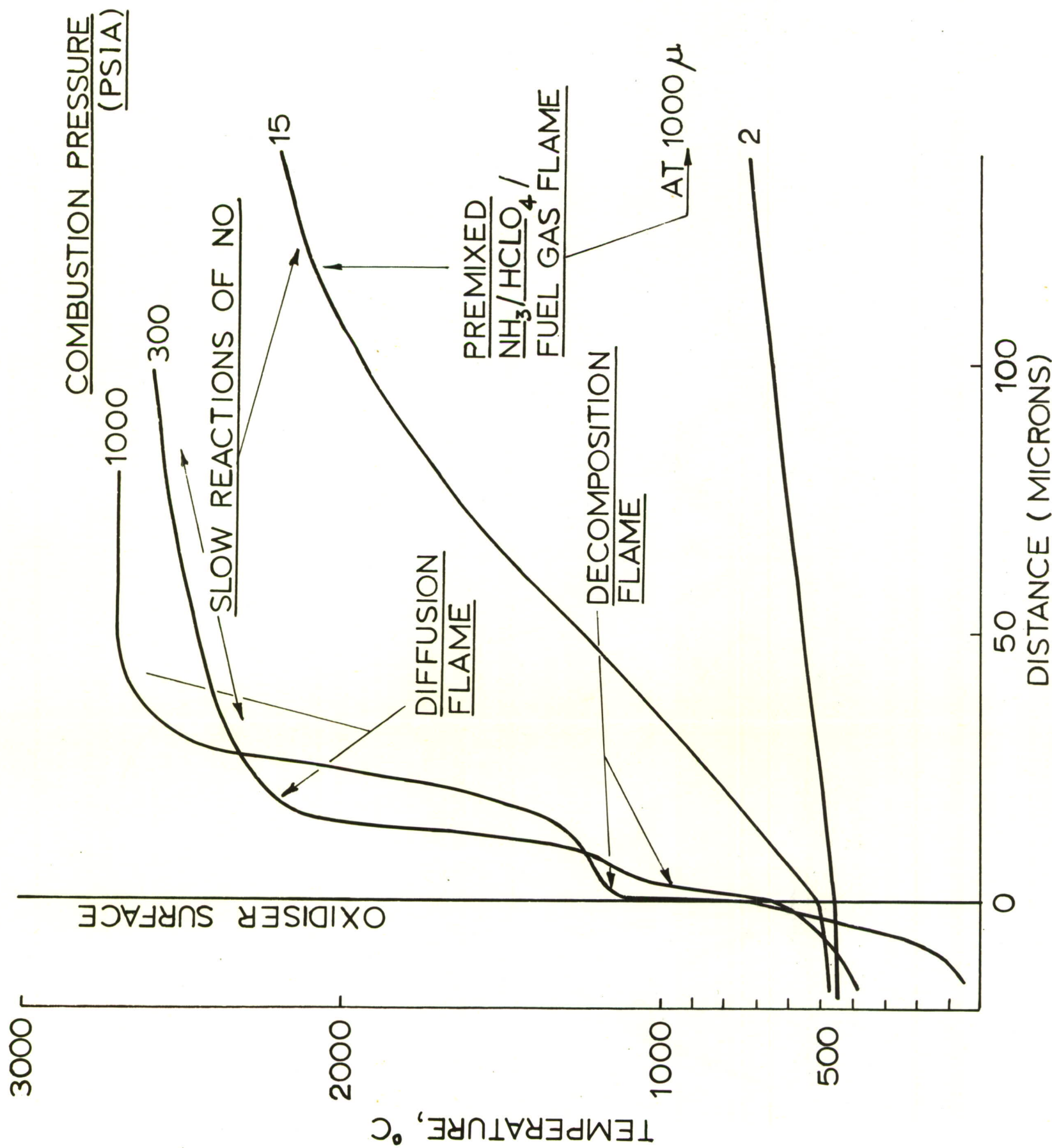


FIG.1B. TEMPERATURE PROFILES VISUALISED FOR AN AMMONIUM PERCHLORATE PROPELLANT (THROUGH OXIDISER CRYSTAL)

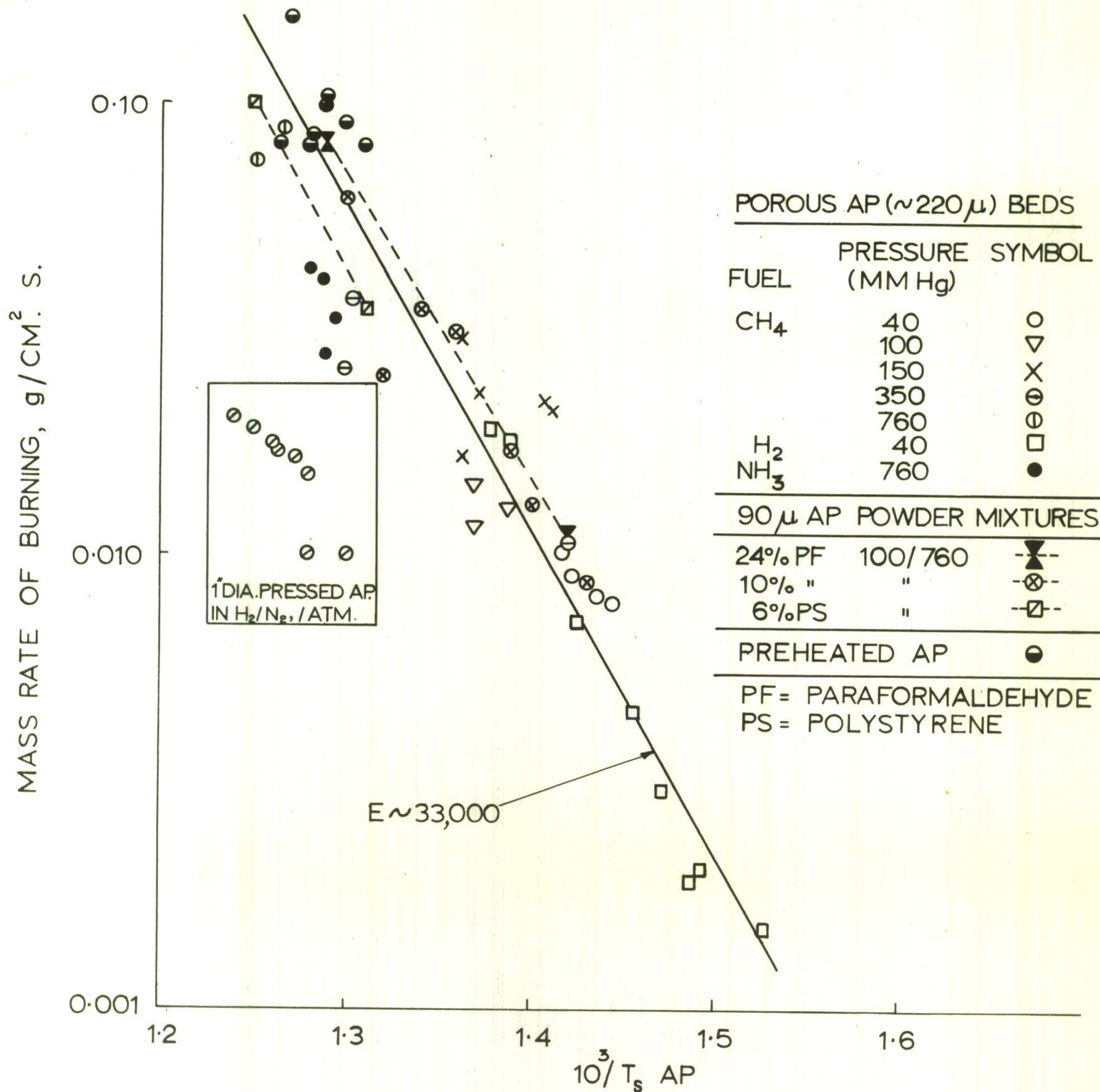
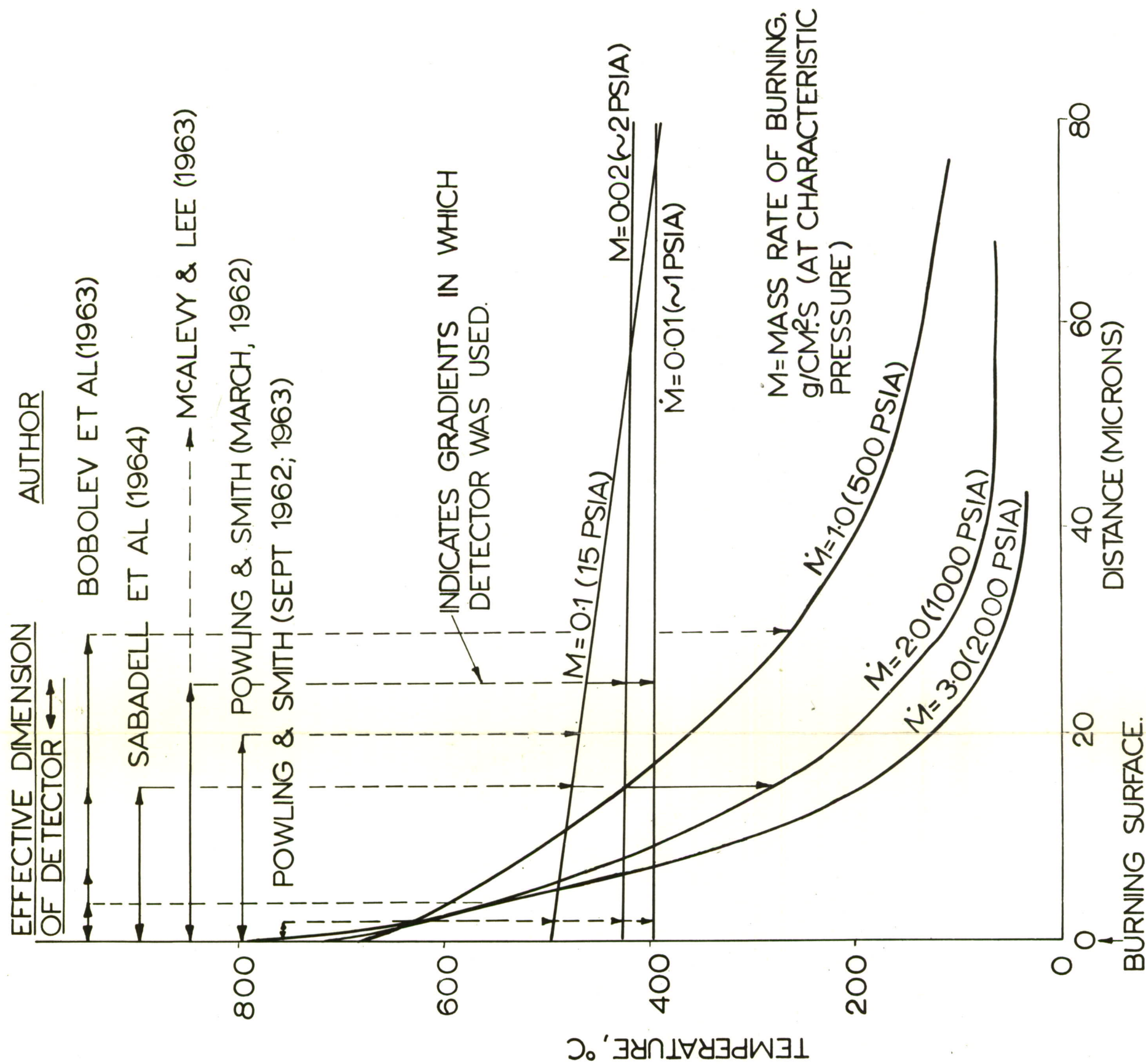


FIG. 2. SURFACE TEMPERATURE / RATE RELATIONSHIP
FOR AMMONIUM PERCHLORATE BURNING
UNDER A VARIETY OF CONDITIONS

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FIG. 3. TEMPERATURE GRADIENTS IN BURNING AMMONIUM PERCHLORATE.

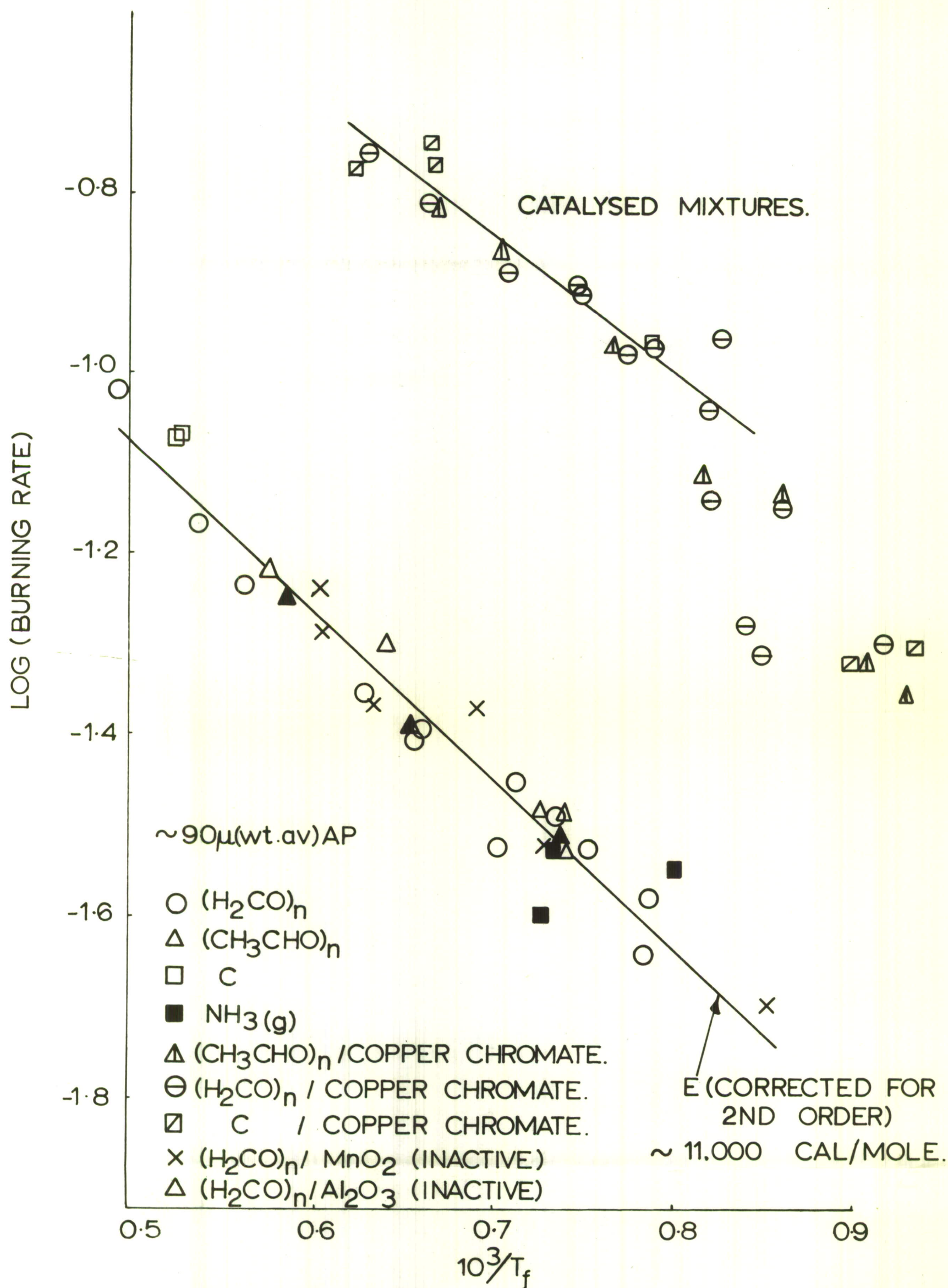


FIG. 4. DEPENDENCE OF BURNING RATE ON MEASURED FLAME TEMPERATURE: WEAK FUEL / AMMONIUM PERCHLORATE MIXTURES AT 1 atm.

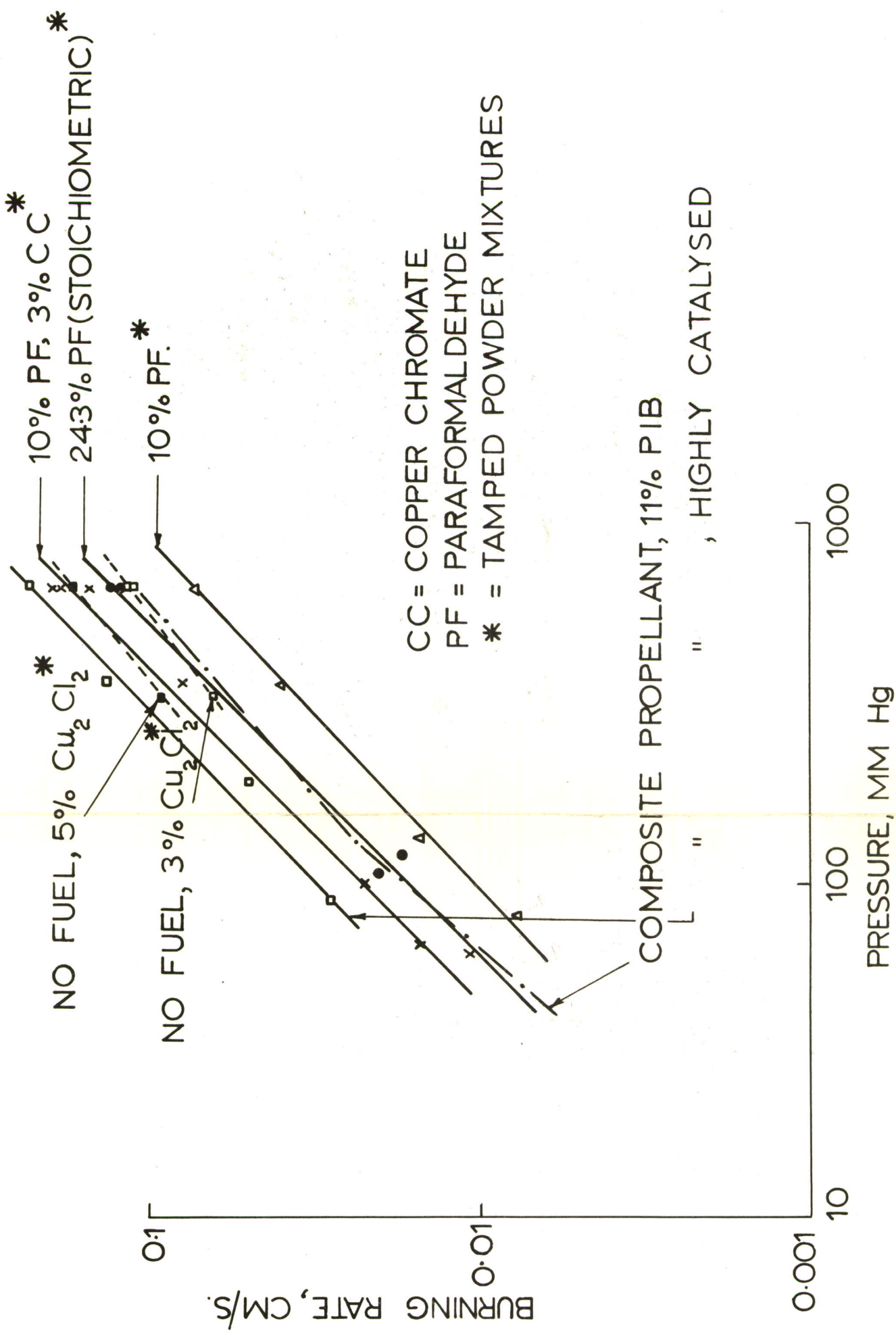


FIG.5. PRESSURE EXPONENT OF CATALYSED COMPOSITIONS.

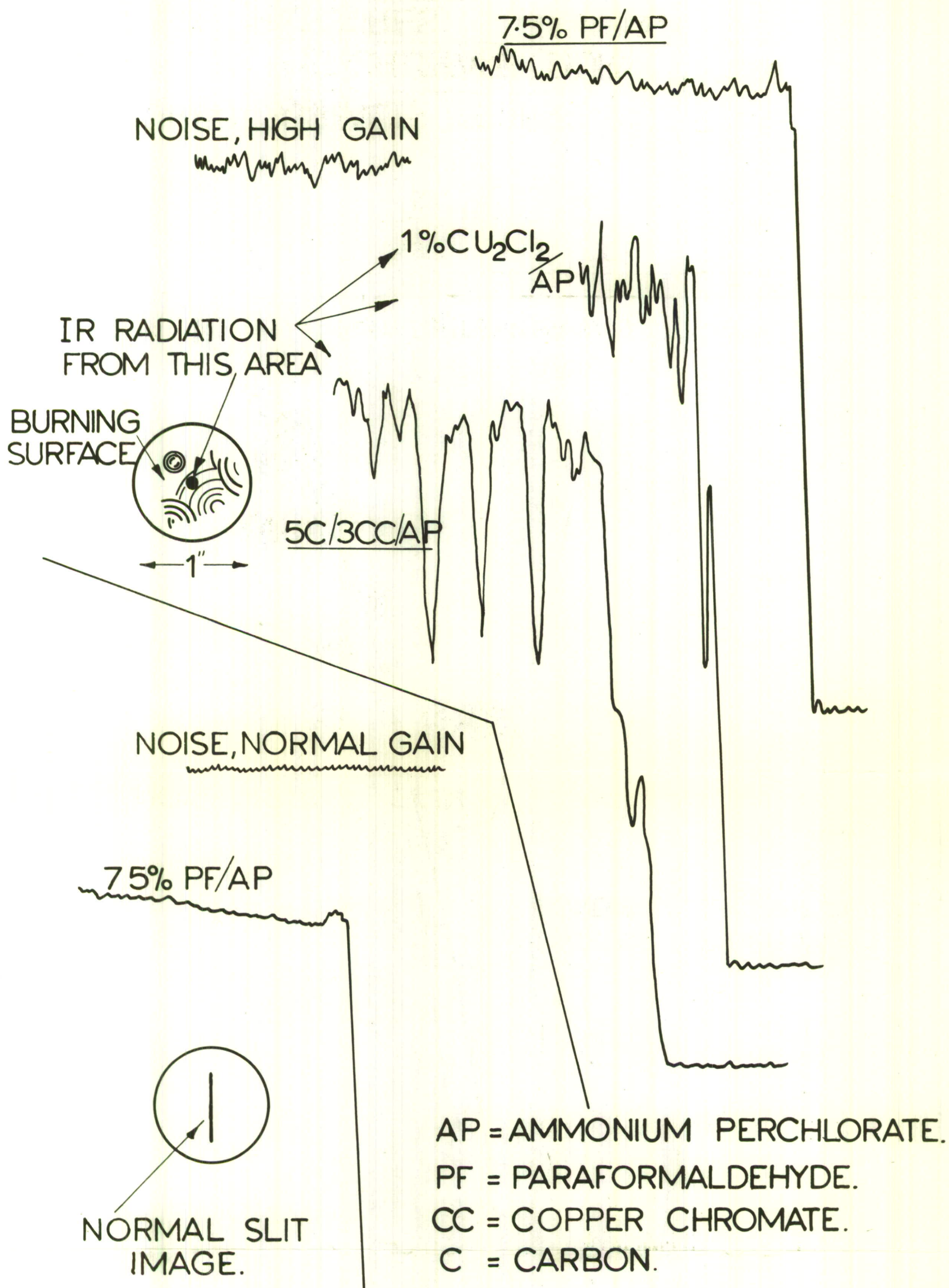


FIG.6. INTENSITY FLUCTUATIONS OF INFRA-RED RADIATION FROM BURNING SURFACES: RECORDER TRACES.

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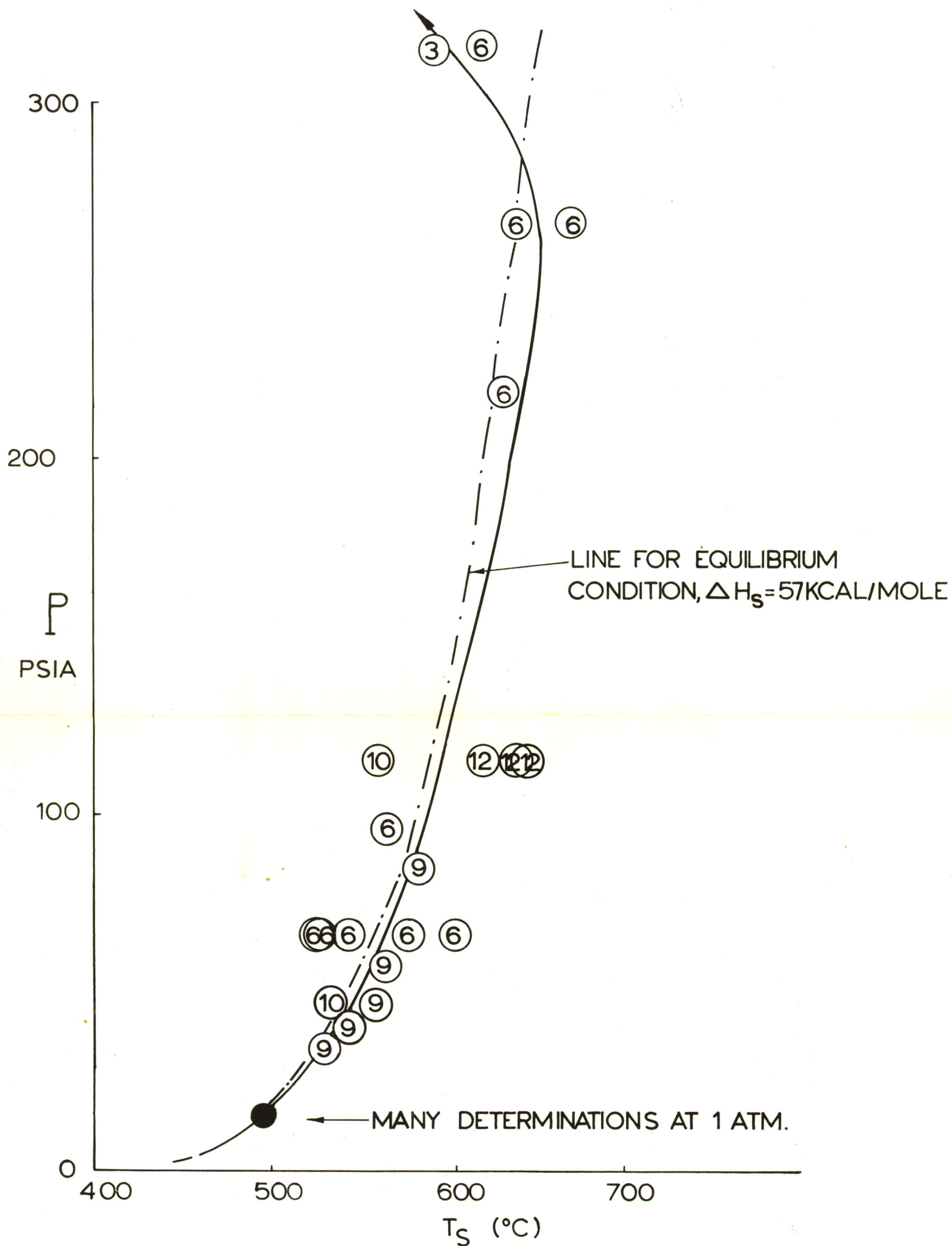


FIG.7. MEASURED SURFACE TEMPERATURE OF AMMONIUM PERCHLORATE BURNING AT ELEVATED PRESSURES.

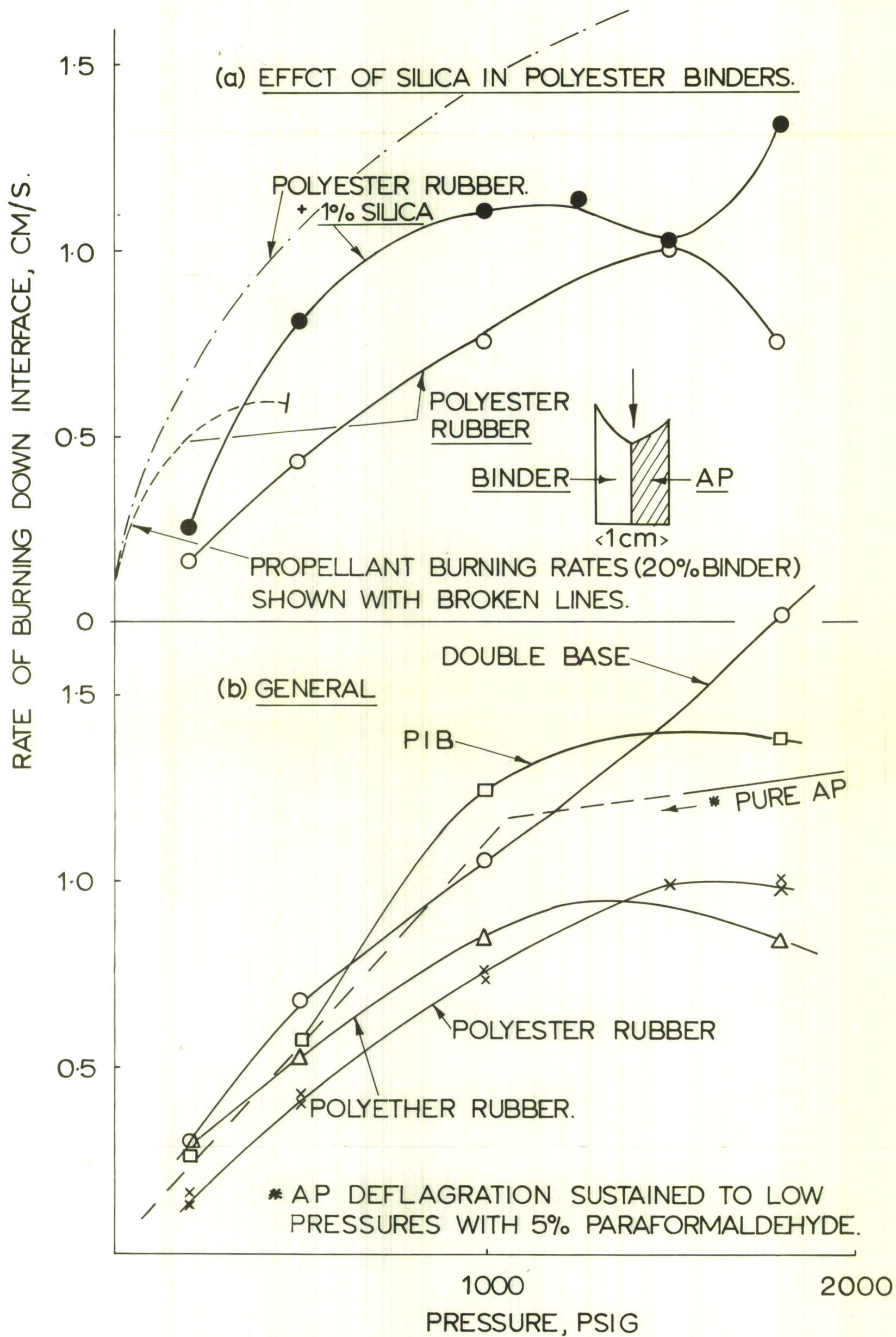


FIG. 8. FLAME PENETRATION DOWN BINDER - OXIDISER INTERFACES.

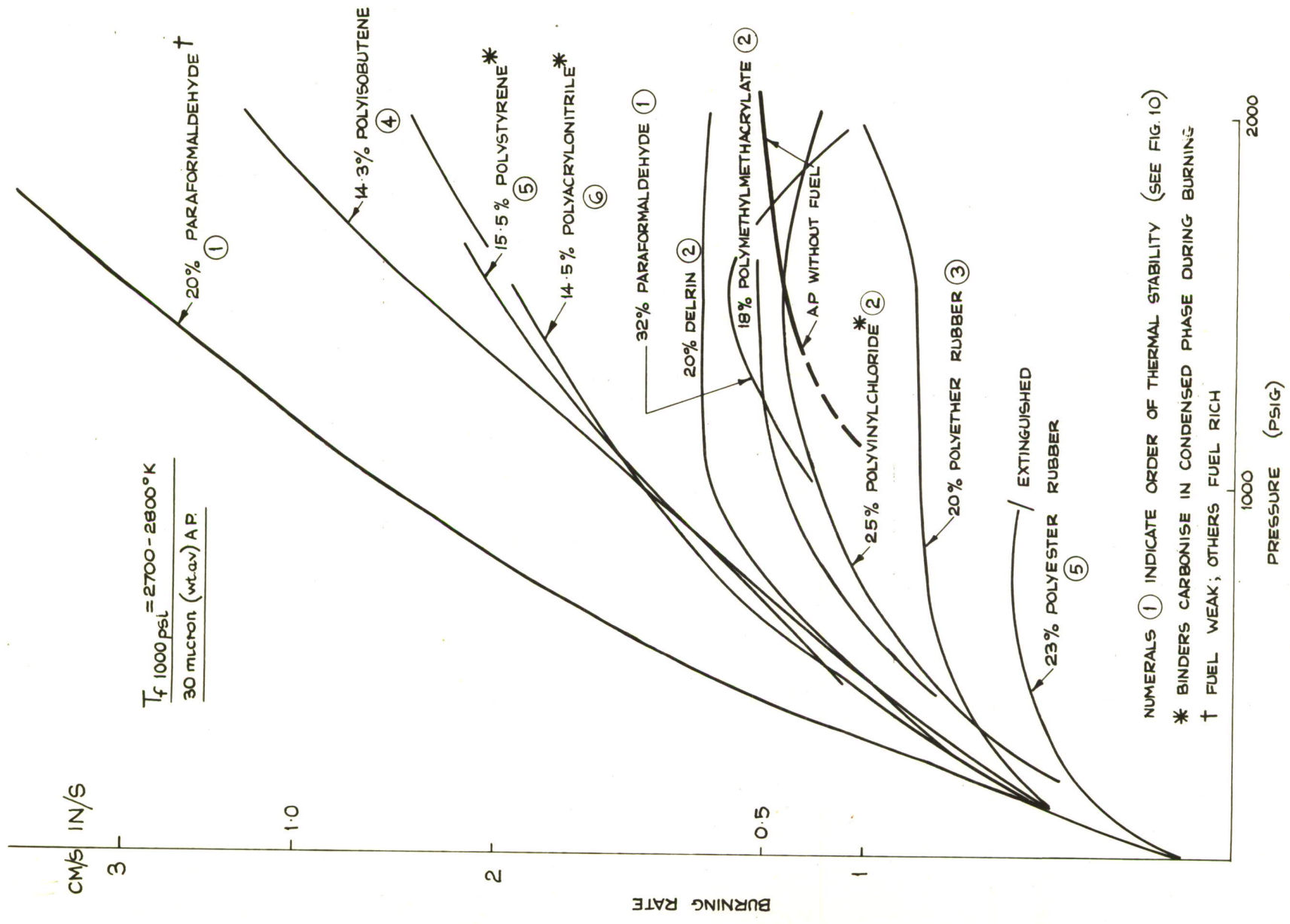


FIG. 9 STRAND BURNING RATES OF AMMONIUM PERCHLORATE COMPOSITIONS CONTAINING DIFFERENT FUELS: CONSTANT FLAME TEMPERATURE AND OXIDISER PARTICLE SIZE.

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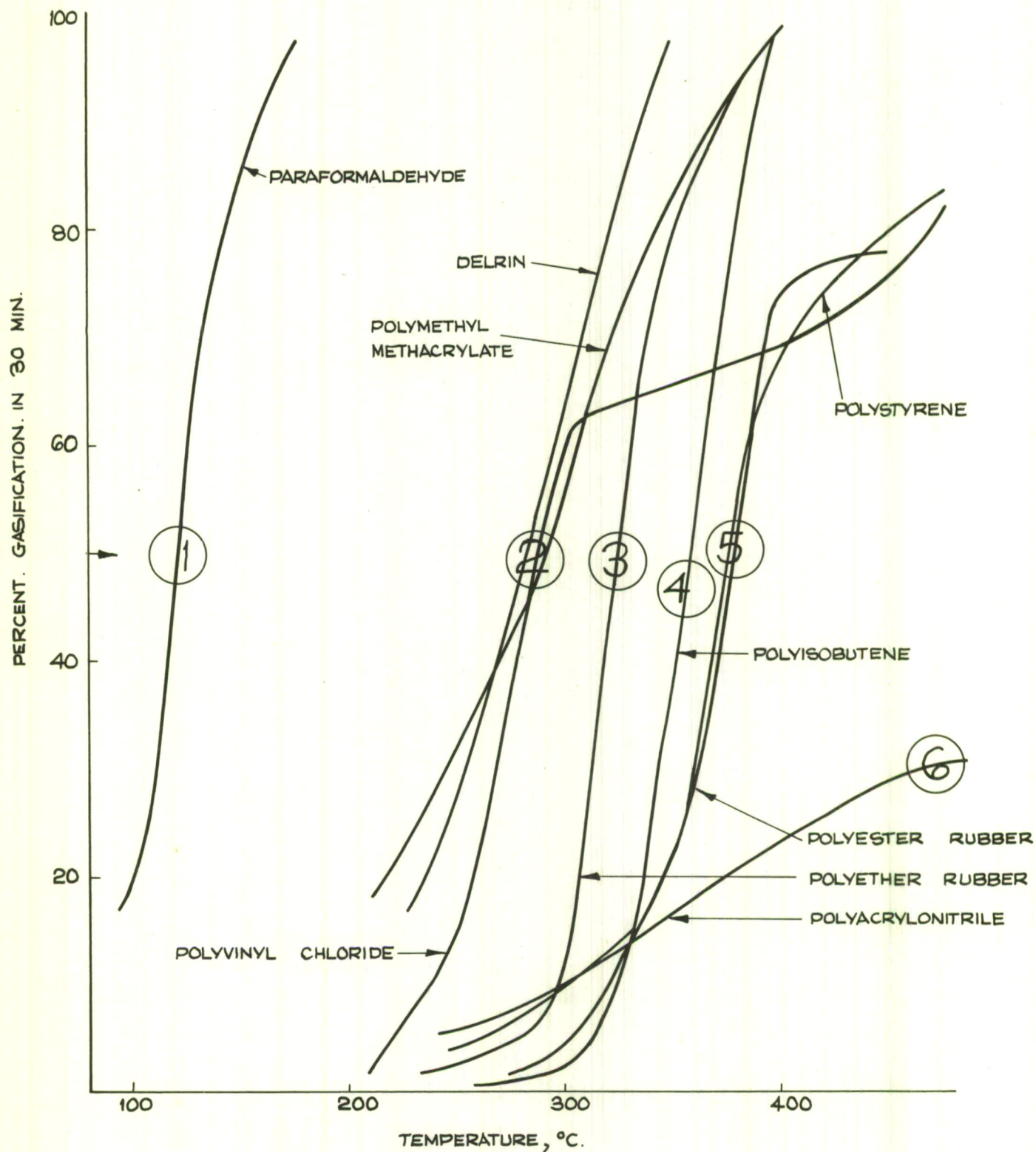


FIG. 10. RELATIVE PYROLYSIS RATES OF POLYMERIC FUELS.

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For most practical propellants burning in the "low pressure" region, the burning rate is probably controlled by a homogeneous premixed gas phase reaction between ammonia, perchloric acid and fuel pyrolysis products. Its very low activation energy is associated with the perchloric acid/fuel reaction; the precise nature of the organic fuel is unimportant. This is in distinct contrast to the strong effect of the chemical nature of the binder in the high pressure region. Some of the possible reasons for this have been explored experimentally, including the penetration of flame down the binder/oxidiser interface and the effect of the thermal stability of the fuel-binder. Some results from experiments on closed vessel pyrolysis and diffusion flame burning of a variety of polymeric fuels are presented.

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